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The reactions of atomic chlorine with acrolein, methacrolein and methyl vinyl ketone

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An investigation into the reactions between Cl atoms and acrolein (1), methacrolein (2) and methyl vinyl ketone (3)

$$\mathrm{CH_2CHCHO + Cl \rightarrow products} \quad (1)$$

$$\mathrm{CH_2C(CH_3)CHO + Cl \rightarrow products} \quad (2)$$

$$\mathrm{CH_2CHC(O)CH_3 + Cl \rightarrow products} \quad (3)$$

is presented. Values of the rate constants for the reactions have been determined by an absolute technique for the first time. At a pressure of 1.6 Torr, the rate constants obtained were: $k_1 = 1.1 \pm 0.2$, $k_2 = 3.3 \pm 0.6$ and $k_3 = 0.99 \pm 0.20$ in units of 10^{-10} cm^3 molecule^{-1} s^{-1}. k_1 was also determined at atmospheric pressure using a relative-rate technique. The rate constant obtained was $(2.2 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}; the larger value compared with that for 1.6 Torr is thought to reflect a true dependence of the reaction rate on pressure. The final products of the reactions performed under an atmosphere of synthetic air were investigated using FTIR spectroscopy. The only chlorinated organic species identified as products of the reactions were chloroacetaldehyde in the case of reaction of Cl atoms with acrolein; chloroacetone with methacrolein; and chloroacetaldehyde with methyl vinyl ketone. Branching ratios for abstraction (the fraction of reactions occurring by abstraction relative to the sum of addition and abstraction processes) were found to be 0.22 ± 0.13 for acrolein, 0.18 ± 0.02 for methacrolein and <0.03 for methyl vinyl ketone. The reaction of Cl atoms with methacrolein proceeds *via* a mechanism that involves the decomposition of the methyl vinyl radical. The decomposition of this radical in synthetic air, and in the absence of NO, appears to lead to the formation of significantly more CO than previously thought. This observation is in agreement with the work of J. J. Orlando, S. E. Paulson and G. S. Tyndall, *Geophys. Res. Lett.*, 1999, **26**, 2191 (ref. 1), who studied the decomposition of the radical under different conditions.

Introduction

The possible role of Cl atoms as important oxidants for organic species in the marine boundary layer has received much attention in recent years. The reactions between sea-salt aerosol and the oxides of nitrogen and ozone are now known to produce species that readily release Cl atoms on photolysis.[2] The fate of these Cl atoms is expected to be reaction either with O_3 or with a volatile organic compound (VOC) to yield HCl or, in the case of unsaturated compounds, a chlorinated organic species.

The α,β-unsaturated-carbonyl compounds acrolein, methacrolein and methyl vinyl ketone are species present in tropospheric air that may react with Cl atoms. The predominant source of methacrolein and methyl vinyl ketone in the troposphere is the oxidation of isoprene. Isoprene is emitted by a huge range of plants and is usually the dominant biogenic VOC emitted from forest sites.[3] Over the oceans, phytoplankton are known to release isoprene directly into the marine boundary.[4] Isoprene reacts rapidly with the OH radical to yield methacrolein and methyl vinyl ketone as major products.[5]

Acrolein is structurally related to methacrolein and methyl vinyl ketone. The main atmospheric source of acrolein is the oxidation of buta-1,3-diene, a component of automobile emissions. Other anthropogenic sources of buta-1,3-diene exist, and the rate of emission of this toxic gas in the urban area of Los Angeles has been estimated at around 26 tonne day^{-1}.[6] A smaller source of acrolein in the atmosphere is its direct release by the polymer industry.[7]

The present paper describes the determination of rate constants and the products of the reactions between atomic chlorine and acrolein, methacrolein and methyl vinyl ketone:

$$\mathrm{CH_2CHCHO + Cl \rightarrow products} \quad (1)$$

$$\mathrm{CH_2C(CH_3)CHO + Cl \rightarrow products} \quad (2)$$

$$\mathrm{CH_2CHC(O)CH_3 + Cl \rightarrow products} \quad (3)$$

The values of the rate constants k_1–k_3 were investigated using the discharge-flow technique at room temperature and at pressures of 1.6 Torr and, in the case of k_1 and k_3, at 4.5 Torr. The value of k_1 was also determined at atmospheric pressure using the relative-rate technique. The final products formed under an atmosphere of synthetic air were determined using FTIR spectroscopy for all three reactions.

Experimental

Discharge-flow studies

The flow tube and other apparatus used for the discharge-flow studies have been described previously.[8] The source of Cl atoms in the flow tube was the reaction of atomic fluorine with HCl:

$$\mathrm{F + HCl \rightarrow HF + Cl} \quad (4)$$

where $k_4 = (1.16 \pm 0.23) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.[9] The flow of molecular fluorine was generally around 10^{16} molecule s^{-1}and the flow of HCl was generally around 10^{18} molecule s^{-1}.

In the case of experiments performed at 1.6 Torr, helium was used as the main flow gas. For the experiments performed at 4.5 Torr, nitrogen was the main flow gas but helium was used to accompany the fluorine gas through the microwave discharge region and therefore composed 24–26% of the total flow. Linear flow velocities of between 18 and 48 m s^{-1} were employed.

Chlorine atoms were detected by resonance fluorescence at $\lambda \sim 138$ nm. The incident light for the resonance fluorescence was supplied by passing a dilute (<4%) mixture of molecular chlorine in helium through a microwave discharge. The best detection limit achieved was 5×10^8 molecule cm^{-3}, for a signal to noise ratio 1 : 1 and an integration time of 5 s.

The reactions were studied under pseudo-first order conditions and the data were treated using the integrated form of the rate equation, $\ln\{[\mathrm{Cl}]_{\mathrm{S}=0}/[\mathrm{Cl}]_t\} = k't$, where S refers to the substrate. The values of k' obtained were corrected to allow for deviations from plug-flow using the expression of Kaufman.[10] Effective coefficients for the diffusion of Cl in He and in mixtures of He and N_2 were calculated using standard expressions (see Massman[11] and Perry and Green[12]) from experimentally determined values of D_0(Ar–He)[13] and $D_0(\mathrm{N_2–N_2})$.[11] With $D_0 = Dp$, and the pressure p expressed in Torr, the values obtained for $T = 298$ K were D_0(Cl–He) = 608 Torr cm^2 s^{-1} and $D_0(\mathrm{Cl–75\%N_2,25\%He}) = 184$ Torr cm^2 s^{-1}.

The concentration of the substrate species was varied in the range $(2.5–18.2) \times 10^{11}$ molecule cm^{-3}, and was always at least a factor of 5 (and up to a factor of 59) greater than the concentration of Cl atoms. The measured pressure was corrected using the Poiseuille equation to allow for the measurement being made at the end of the contact distance, rather than in the middle. This correction to the pressure was 4–7%.

Relative-rate measurements

We describe in this paper the determination of k_1 by the relative-rate technique. Relative-rate measurements have previously been employed by us to obtain values of k_2 and k_3,[14] and, as the method used is the same as that described in some detail in our publication, only a brief description is given here.

The basis of the relative-rate technique is that loss of the substrate species is monitored and compared to that of a reference compound over an identical time in the presence of the co-reactant, Cl atoms in this case. If reaction with Cl atoms is the only loss route for the substrate, S, and reference, R, compounds, then the relevant equations are

$$\text{substrate} + \mathrm{Cl} \rightarrow \text{products} \quad (5)$$

$$\text{reference} + \mathrm{Cl} \rightarrow \text{products} \quad (6)$$

and the concentrations of substrate and reference species are described by the equation

$$\ln \frac{[\mathrm{S}]_{t=0}}{[\mathrm{S}]_t} = \frac{k_\mathrm{S}}{k_\mathrm{R}} \ln \frac{[\mathrm{R}]_{t=0}}{[\mathrm{R}]_t} \quad (\mathrm{I})$$

According to eqn. (I), a plot of $\ln\{[\mathrm{S}]_{t=0}/[\mathrm{S}]_t\}$ *vs.* $\ln\{[\mathrm{R}]_{t=0}/[\mathrm{R}]_t\}$ should give a straight line of slope $k_\mathrm{S}/k_\mathrm{R}$. Provided that the value of k_R is known, the value of k_S may thus be calculated.

The relative-rate experiments were carried out at atmospheric pressure using a collapsible 50 l PTFE reaction chamber (Alltech). All experiments were conducted at 299 ± 2 K. The concentrations of the substrate and reference species were monitored using a gas-chromatograph with a flame-ionisation detector (SRI, 8500). A 5 cm^3 sample loop and a SuperQ column (Alltech) was used. The column was held at 80 °C for 45 min and then heated to 150 °C and held there for 5 min.

Propane was used as the reference compound. The source of atomic chlorine was the photolysis of molecular chlorine. The radiation was provided by two 30 W 'black-lamps' (NIS FL30-BLB) with a peak output at around $\lambda = 365$ nm and essentially no emission below 300 nm. The concentration of molecular chlorine initially present in the reaction chamber was $(1–3) \times 10^{14}$ molecule cm^{-3}, whilst the concentrations of acrolein and propane were varied with respect to each other within the limits of $(1.3–3.5) \times 10^{14}$ molecule cm^{-3}. Four different reaction mixtures were prepared, three using nitrogen as the bath gas and one using synthetic air. No loss of the substrate material was observed over the photolysis times used in the absence of $\mathrm{Cl_2}$, and, with the concentrations of reagents used, no reaction between acrolein and $\mathrm{Cl_2}$ in the dark was observed over the timescale of a whole experiment.

In order to assess the error associated with the measurement of the substrate and reference compounds, a mixture containing the average initial concentration of acrolein and propane was repeatedly sampled a total of six times. The standard deviation of this set of measurements was taken to be representative of the errors in all concentration measurements.

Product detection by FTIR spectroscopy

The final products formed by the reaction of Cl atoms with acrolein, methacrolein and methyl vinyl ketone in synthetic air were investigated by Fourier-transform infra-red (FTIR) spectroscopy.

The reactions were studied at atmospheric pressure and room temperature. The reaction chamber used was a 56 l PTFE bag housed in a dark chamber. The photolysis of molecular chlorine was again used as the source of Cl atoms.

The spectrometer used was a single beam ATR Mattson Infinity FTIR spectrometer with a deuterated triglyceride sulfate detector. WinFirst® software (ATR-Mattson) was used to manipulate all files. The cell used was a 5.6 l Wilks cell with internal gold-coated focusing mirrors. The total folded pathlength employed was 11.25 m. The beam of IR radiation passed through laboratory air before entering and on leaving the cell. All spectra obtained, including background spectra, were taken at 2 cm^{-1} resolution, and represent the average of 200 scans. The 200 scans took just under 11 min to collect.

The reagents in the reaction chamber were allowed to mix for 2 h in the dark before a spectrum of the contents of the bag was recorded. The lights were switched on for between 10 and 60 s and a spectrum of the contents of the bag after photolysis was recorded. The process of illumination followed by recording a spectrum was repeated a further 5 times on average. The maximum consumption of the substrate species was never more than 30%.

The product spectrum was a convolution of the spectra of all the reaction products with a minor amount of interference due to atmospheric CO_2 and H_2O. The absorbance due to CO was in all cases uncomplicated, so that the concentration of CO could be found by measuring the absorbance between 2238 and 2015 cm^{-1}. The concentrations of all other species in the sample were obtained by subtracting out a reference spectrum of the compound of interest.

Calibrations were performed by flushing a known amount of the species into the bag and adding synthetic air until the bag contained 50 l of gas. The contents of the bag were allowed to mix for 2 h before a spectrum of the mixture was recorded. Table 1 gives the absorption features used to obtain the calibration plots.

The error in measuring the concentration of each species was determined in a manner analogous to that described for chromatographic analysis in the relative-rate studies.

Of the reactions investigated, that between Cl atoms and methacrolein, reaction (2), was the most thoroughly studied. The initial concentrations of methacrolein and molecular chlorine were varied in separate experiments (see Table 2). However, the fractional yields of the various products were independent of these initial concentrations.

Initial concentrations, in units of 10^{15} molecule cm^{-3}, used in the study of the other reactions were [acrolein] = 1.4 and 1.7 for reaction (1) and [methyl vinyl ketone] = 1.4 and 2.1 for reaction (3). Initial Cl_2 concentrations were 1.7×10^{15} molecule cm^{-3} in all these experiments. Test reactions were performed with all three substrates to ensure that reaction with Cl_2 or photolysis of the substrate did not occur over the timescale of an experiment.

Materials

The gases used for the main flow gas in the discharge-flow experiments, nitrogen (BOC, 99.9%) and helium (BOC, 99.996%), and the helium used for the resonance-fluorescence lamp (BOC, 99.999%) were passed through a mixture of molecular sieves (BDH, 4A, 5A and 13X) held at either liquid N_2 or solid CO_2 temperature before use. The bath gases for the relative-rate experiments, nitrogen (BOC, 99.9%) and synthetic air (BOC, 99.9% (80% N_2, 20% O_2)) were passed through molecular sieves 4A, 5A and 13X (BDH) cooled by solid CO_2, before use. The gases used for the gas chromatography were hydrogen (BOC, 99.9%), synthetic air (BOC, 99.9% (80% N_2, 20% O_2)) and helium (BOC, 99.999%). The synthetic air ((99.9% (80% N_2, 20% O_2)) used for the FTIR product studies was supplied by BOC and passed through P_2O_5 before use.

HCl (Aldrich, 99.5 + %), chlorine (BDH, 99.9%), chloroacetaldehyde (Aldrich, 50% by weight solution in water), propane (BOC, 99.5%), and the acrolein used for the relative-rate experiments (90%, <10% H_2O and cyclic dimer, hydroquinone stabiliser) were subjected to freeze–pump–thaw cycles before use. The acrolein used for the discharge-flow and product studies (Supelco, neat EPA), methacrolein (Aldrich, 95%, stabilised), methyl vinyl ketone (Aldrich, 99%, 0.1% acetic acid, 0.05% hydroquinone) and chloroacetone (Aldrich, 95% with 0.5% $CaCO_3$), were purified by trap-to-trap distillation under vacuum before use. Only the middle third of the vapour which came off the sample was used. Formaldehyde was prepared by pyrolysing a degassed solid sample of paraformaldehyde (Aldrich, 95%); the vapour released upon heating was used without any further purification. Fluorine (Messer 1% in 99.999% He) and CO (Aldrich, 10% in helium, calibration mixture) were used as supplied.

Table 1 Absorption features used to obtain calibration plots

Compound	Absorption band/cm^{-1}
Acrolein	1779–1658
Methacrolein	778–872
Methyl vinyl ketone	1767–1658
Chloroacetone	1303–1113
Formaldehyde	1815–1583
CO	2238–2015

Table 2 Initial concentrations of methacrolein and Cl_2 used

[Methacrolein]/molecule cm^{-3}	[Cl_2]/molecule cm^{-3}
5.0×10^{15}	0.8×10^{15}
4.0×10^{15}	2.5×10^{15}
2.6×10^{15}	1.3×10^{15}
1.0×10^{15}	2.5×10^{15}

Results and discussion

Kinetic studies

Second-order rate constants were obtained for reactions (1), (2) and (3) at a pressure of 1.6 Torr. In addition, values of k_1 and k_3 were also determined at a pressure of 4.5 Torr. A typical first-order plot for the reaction of acrolein with Cl atoms obtained at 1.6 Torr is shown in Fig. 1; the apparent negative intercept is a consequence of an offset in the zero-time reference. Second-order plots are exemplified by Fig. 2 for reaction (2) at 1.6 Torr and Fig. 3 for reaction (3) at 4.5 Torr. Small negative and positive intercepts were observed in these second-order plots, but they were all smaller than the 95% confidence limits on these intercepts. There are arguments in favour of using the floating-intercept analysis rather than forcing the lines through the origin, but, in reality, the differences in slopes obtained are smaller than the errors. Table 3 gives the values of the rate constants obtained from the slopes of the second-order plots; the errors represent the 95% confidence limits.

The relative-rate plot for reaction (1) is shown in Fig. 4. The straight line drawn through the points is the result of a weighted least-squares regression that takes into account the errors in both the axes.[16]

The value of k_1/k_R obtained was 1.59 ± 0.07. Using a value of $k_R = (1.37 \pm 0.11) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1},[17] for the reaction of Cl atoms with propane, yields $k_1 = (2.2 \pm 0.3) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}. The error quoted incorporates both the 95% confidence limits from the slope and the quoted error in the value of the rate coefficient for the reference compound. Table 3 shows how the values obtained by the discharge-flow technique compare with the values obtained by the relative-rate technique.

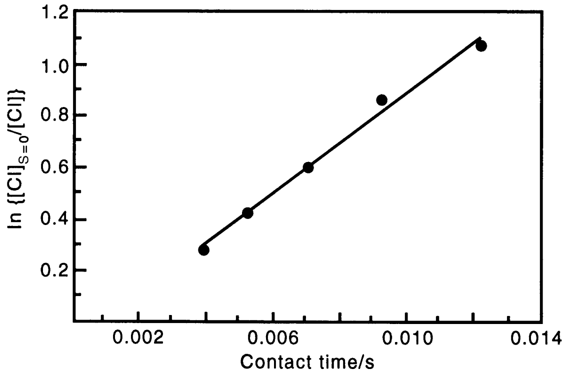


Fig. 1 Typical first-order plot obtained for the reaction of Cl atoms with acrolein at $P = 1.6$ Torr.

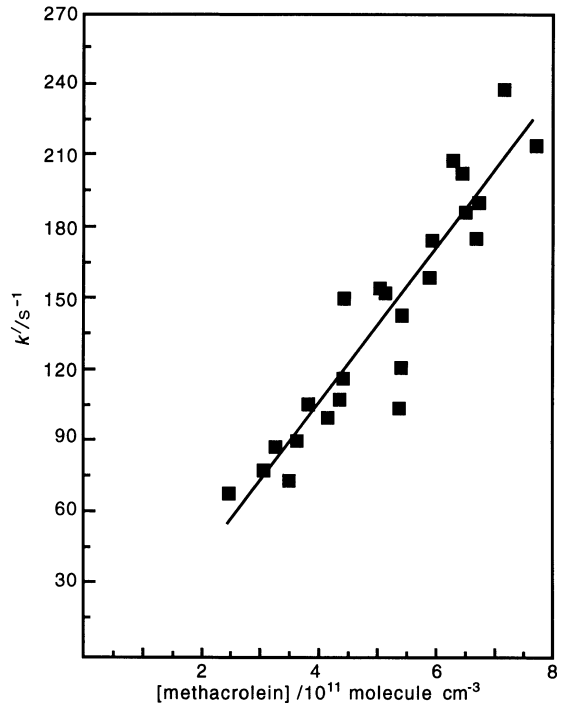


Fig. 2 Second-order plot obtained for the reaction of Cl atoms with methacrolein at $P = 1.6$ Torr.

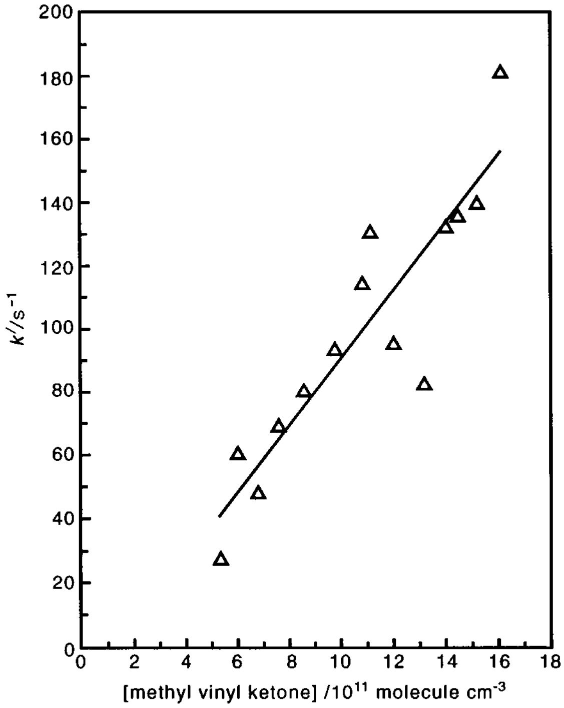


Fig. 3 Second-order plot obtained for the reaction of Cl atoms with methyl vinyl ketone at $P = 4.5$ Torr.

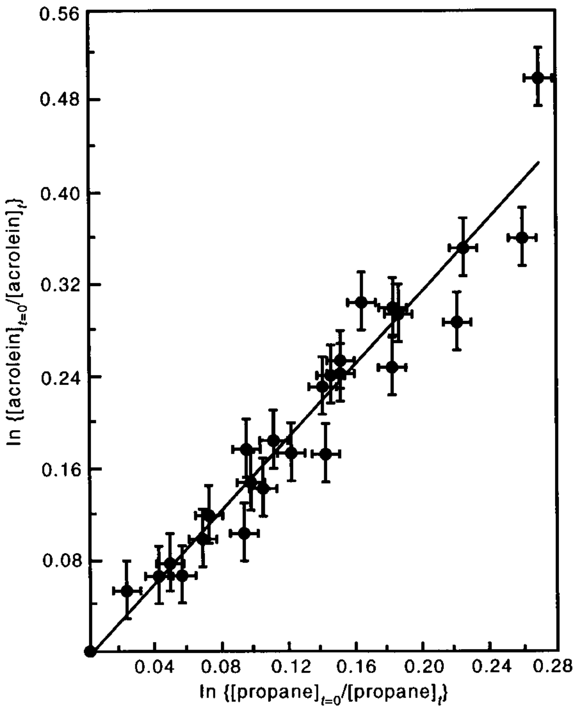


Fig. 4 Relative-rate plot for the reaction of Cl atoms with acrolein; propane was used as the reference compound.

It can be seen from Table 3 that only in the case of methacrolein is the value obtained at atmospheric pressure the same within error as that obtained at ~1.6 Torr. There is no obvious reason why the values determined by the discharge-flow method should be erroneously low, especially since the measurements have been corrected for deviations from plug flow. The value of k_3 obtained by our implementation of the relative-rate technique[14] agrees with the value obtained by the same technique by Finlayson-Pitts *et al.*[15] These latter workers used *n*-nonane as the reference compound, so that the agreement suggests that the value adopted by us for k_R for propane is correct. No values for k_1 or k_2 have previously been reported in the literature.

The results of the present work seem to indicate that the rate coefficients for the reactions of Cl with acrolein and with methyl vinyl ketone are slightly dependent on the pressure in the range 1.6 and 760 Torr, although the rate coefficients obtained at 1.6 Torr are a factor of only ~2 smaller than the values obtained at atmospheric pressure. The reason why reaction of Cl with methacrolein does not, in contrast, exhibit a significant pressure effect may be attributed to the structure of methacrolein. With a more substituted carbon–carbon double bond than acrolein or methyl vinyl ketone, methacrolein is more readily stabilised following the addition of chlorine. This proposed greater stability of the

Table 3 Comparison of values obtained for k_1–k_3 using the discharge-flow and relative-rate technique

	Discharge-flow		Relative-rate
	1.6 Torr in He /cm^3 $molecule^{-1}$ s^{-1}	4.5 Torr in N_2 and He /cm^3 $molecule^{-1}$ s^{-1}	~760 Torr in N_2 or air /cm^3 $molecule^{-1}$ s^{-1}
Acrolein	$(1.1 \pm 0.2) \times 10^{-10}$	$(1.4 \pm 0.4) \times 10^{-10}$	$(2.2 \pm 0.3) \times 10^{-10}$
Methacrolein	$(3.3 \pm 0.6) \times 10^{-10}$	—	$(3.2 \pm 0.5) \times 10^{-10}$[a]
Methyl vinyl ketone	$(9.9 \pm 2.0) \times 10^{-11}$	$(1.1 \pm 0.3) \times 10^{-10}$	$(2.1 \pm 0.5) \times 10^{-10}$[a] $(2.0 \pm 0.2) \times 10^{-10}$[b]

[a] Ref. 14. [b] Ref. 15.

Cl–methacrolein adduct is consistent with recent *ab initio* calculations (J. N. Harvey, University of Bristol, personal communication). At the B3LYP/DZP density functional level of theory, the addition energy for the methacrolein reaction is found to be −103.9 kJ mol^{-1}, compared to −95.4 kJ mol^{-1} for the reaction with acrolein and −98.0 kJ mol^{-1} for the reaction with methyl vinyl ketone. Similar trends are observed at the MP2/DZP and CCSD(T)/DZP/B3LYP/DZP levels of theory. It would appear that the slightly more exothermic nature of the addition reaction between Cl and methacrolein causes the reaction to reach its high-pressure limit at a somewhat lower pressure than do the reactions of the other two carbonyl species.

Products

Methacrolein. The identified products of reaction (2) between Cl atoms and methacrolein in synthetic air at atmospheric pressure were chloroacetone, formaldehyde, CO and HCl. Fig. 5 shows a typical spectrum of the starting material, the mixture after photolysis and the spectrum of the reaction products. Fig. 6 shows how the concentration of these species changed with time of photolysis.

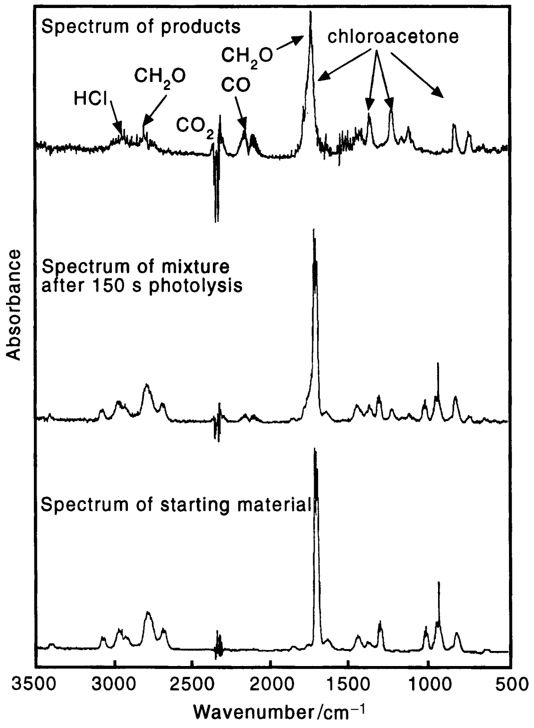


Fig. 5 Typical IR-spectra of the starting materials, the mixture after photolysis, and the reaction products, for the reaction of Cl atoms with methacrolein.

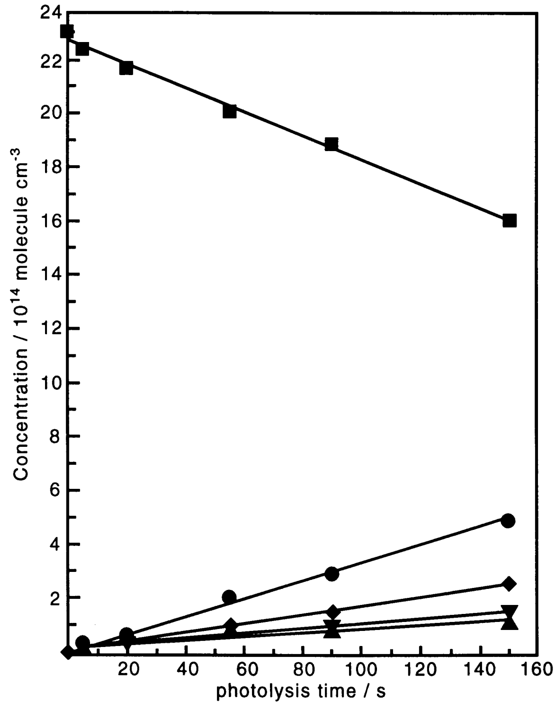


Fig. 6 Change in concentration of methacrolein (■) and the products: chloroacetone (◆), formaldehyde (▼), CO (●) and HCl (▲) with time for the reaction of Cl atoms with methacrolein.

Atomic chlorine may react with the products of reaction (2). The reactions of Cl with HCl, CO and chloroacetone all possess very small rate coefficients compared to that for reaction (2).[18,19] However, the value of the rate constant for the reaction of Cl atoms with formaldehyde is 7.3×10^{-11} cm^3 molecule^{-1} s^{-1},[20] a factor of only ~4 less than the value of k_2. One of the products of the reaction is HCl. A small correction was made to the yield of formaldehyde and HCl to allow for the loss of formaldehyde due to reaction with Cl. The correction was made according to a method suggested by Atkinson *et al.*[21] These workers proposed that the concentration of a product species measured, $[A]_t$, could be adjusted by multiplying by a factor, F, to give the concentration of A which would have been present if the species did not go on to react further in the system, $[A]_0$. The relevant reactions for this work are reaction (2), the reaction of Cl atoms with methacrolein, and the reaction

$$CH_2O \rightarrow HCl + CHO \qquad (7)$$

Note that the CHO radical formed will react subsequently with O_2 to form CO and HO_2.

The relevant equation is therefore

$$\Delta[CH_2O]_0 = F\Delta[CH_2O]_t \qquad (II)$$

where the correction factor F is defined by Atkinson *et al.* as

$$F = \frac{k_2 - k_7}{k_2}\left\{\frac{1 - \dfrac{[\text{methacrolein}]_t}{[\text{methacrolein}]_0}}{\left(\dfrac{[\text{methacrolein}]_t}{[\text{methacrolein}]_0}\right)^{k_7/k_2} - \dfrac{[\text{methacrolein}]_t}{[\text{methacrolein}]_0}}\right\} \qquad (III)$$

The value of F was calculated for each $\Delta[CH_2O]$ point measured. The correction increased the overall yield of formaldehyde by only ~1% (absolute correction). The reaction of Cl atoms with formaldehyde yields HCl and CO. The yields of these two products were corrected to take into account the small percentage formed by reaction (7) rather than reaction (2).

Increases in the concentration of each identified reaction product were plotted as a function of the decrease in the concentration of methacrolein. Fig. 7 shows an example, Δ[chloroacetone] displayed as a function of −Δ[methacrolein]. The slopes of these plots give the fraction of the reaction that yielded each particular product. The intercept of all plots such as that displayed in Fig. 7 is in every case zero at the 95% confidence level. As for Fig. 4, the regression analysis is a special one[16] that allows for errors in abscissa as well as ordinate.

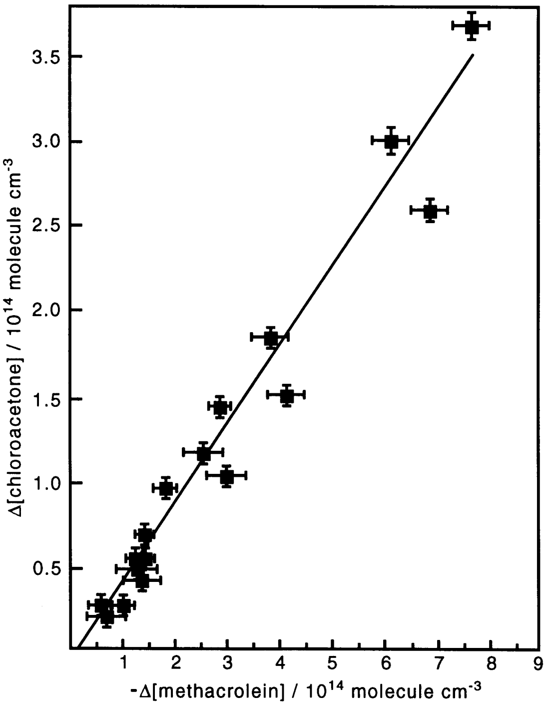


Fig. 7 Plot of Δ[chloroacetone] *vs.* −Δ[methacrolein] for the reaction of Cl atoms with methacrolein.

The yields obtained for the various identified products of reaction (2) between methacrolein and atomic chlorine are shown in Table 4. The errors quoted for the yields incorporate concentration errors for each compound as determined from the repeated sampling of the species and the precision error implicit in the subtraction procedure.

The carbon mass balance obtained for the observations for reaction (2) is only 59 ± 5%. Subtraction of chloroacetone, formaldehyde, CO and HCl from the product spectrum reveals the presence of other absorption features. The species responsible for these residual absorption bands have not been identified, although the species (or one of the species) clearly contains a carbonyl functional group.

The products of reaction (2) were also studied using a gas chromatograph equipped with a flame-ionisation detector. A Chromosorb 101® packed column (Alltech) was used. Only one clear product peak was observed and this peak was found to correspond to chloroacetone.

Acrolein. The products of reaction (1) between Cl atoms and acrolein as determined by FTIR spectroscopy were HCl, chloroacetaldehyde, formaldehyde and CO. Formyl chloride was not observed. Fig. 8 shows a typical spectrum of the starting materials, the mixture after photolysis, and the resultant spectrum of the products. The FTIR spectrum showed evidence of other products, but the composition of these products was not determined. The only product clearly identified by GC analysis was chloroacetaldehyde.

The yield of HCl was 0.22 ± 0.13, at the 95% confidence limits, the large error reflecting the very small sample size. The yield of CO was found to be 0.93 ± 0.53 at the 95% confidence limits.

Table 4 Yields for the formation of identified products in the reaction of Cl with methacrolein

Product	Yield
Chloroacetone	0.46 ± 0.04
Formaldehyde	0.23 ± 0.02
CO	0.75 ± 0.06
HCl	0.18 ± 0.02

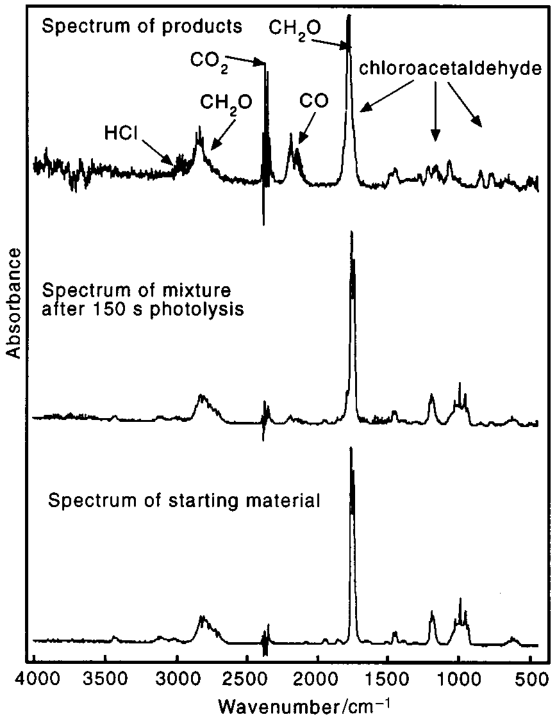


Fig. 8 Typical IR-spectra of the starting materials, the mixture after photolysis, and the reaction products, for the reaction of Cl atoms with acrolein.

Methyl vinyl ketone. The products of reaction (3), as identified by FTIR spectroscopy, were chloroacetaldehyde, formaldehyde and CO. Fig. 9 shows a typical spectrum of a starting mixture, a mixture after photolysis, and a spectrum of the products observed. Again, there was evidence of other products. Gas-chromatographic analysis gave one major product peak with a retention time the same as that of chloroacetaldehyde; numerous smaller peaks were also observed.

The yield of CO observed was very low, ~0.05. HCl was not observed as a reaction product, and we estimate an upper limit of the yield for HCl production of 0.03 on the basis of our detection limits for this species.

Discussion of mechanisms

Methacrolein. Scheme 1 shows that a series of steps leads to the formation of a chloroperoxy radical that can be further converted by reaction with any of the organic peroxy species present in the system to a chloroalkoxy radical. Three pathways for the decomposition of this radical can be envisaged, leading to the product pairs (i) CHO + $ClCH_2C(O)CH_3$ (chloroacetone); (ii) CH_2Cl + $CH_3C(O)CHO$ (methyl glyoxal); and (iii) CH_3 + $ClCH_2C(O)CHO$ (chloromethyl glyoxal). Channel (i) is thermodynamically 84 kJ mol^{-1} more favourable than channel (ii) and 95 kJ mol^{-1} more favourable than channel (iii) according to the heats of formation of the molecules calculated using Benson's rules[22] and the values recommended by DeMore *et al.*[18] for the heats of formation of the radical species.

Chloroacetone, the only product that unambiguously derives from the addition pathway, is thus also the product of

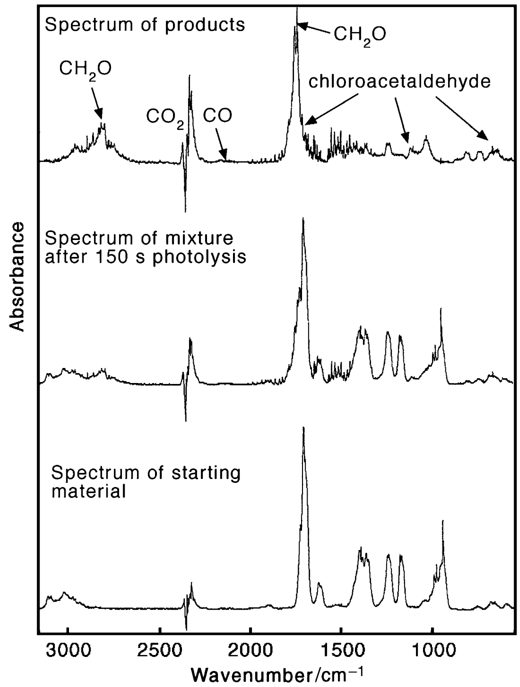
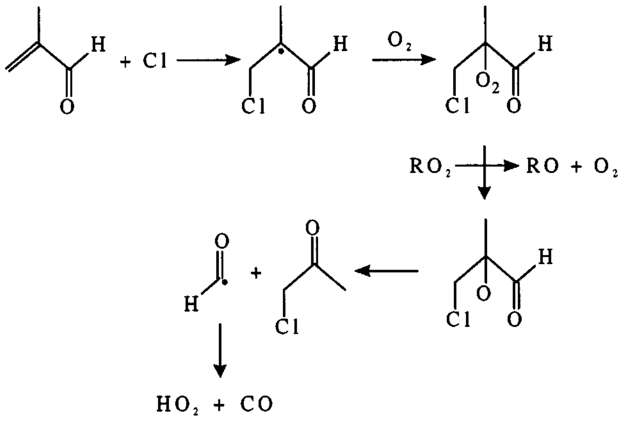


Fig. 9 Typical IR-spectra of the starting materials, the mixture after photolysis, and the reaction products, for the reaction of Cl atoms with methyl vinyl ketone.

the most thermodynamically probable channel. However, the yield of chloroacetone was 0.46 ± 0.04. The yield of HCl was 0.18 ± 0.02, indicating that a fraction 0.82 of the reaction proceeds *via* an addition mechanism. An addition mechanism that does not give chloroacetone must therefore account for a proportion (0.82–0.46) = 0.36 of the reaction.

Chloromethyl radicals, CH_2Cl, from channel (ii) would lead to formyl chloride in the system. Neither formyl chloride nor methyl glyoxal were observed as reaction products, so that there is no evidence for the participation of channel (ii). Methyl radicals, CH_3, from channel (iii) would react further in the system to give formaldehyde. Formaldehyde was observed as a reaction product. Other sources of formaldehyde in the system exist, however, so that the decomposition of the alkoxy radical to yield CH_3 and chloromethyl glyoxal cannot be confirmed.

It thus appears to us that the unidentified addition products might not result from the decomposition of the chloroalkoxy radical shown in Scheme 1, but instead result from reactions of the chloroperoxy radical (such as reaction with HO_2) that do not yield the chloroalkoxy radical, or they might follow addition of chlorine to the more hindered end of the double bond.

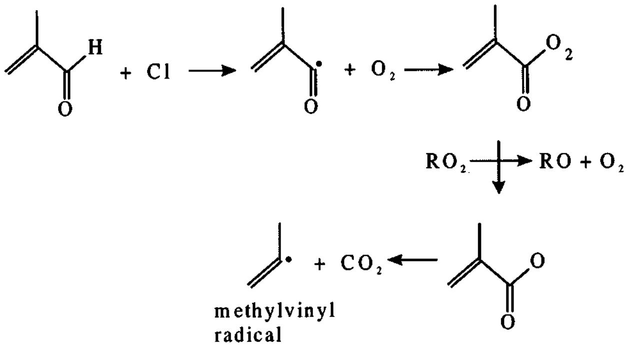


Scheme 1

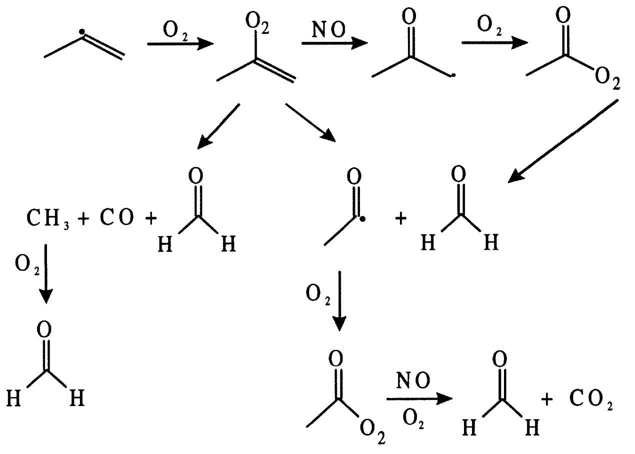
The yield of CO was 0.75 ± 0.04, indicating that channel (i) of Scheme 1 cannot represent the only route by which CO is formed. A pathway, or pathways, must exist which gives rise to a yield of CO of (0.75 − 0.46) = 0.29. The presence of HCl demonstrates the occurrence of hydrogen abstraction, presumably of the labile aldehydic hydrogen. The methyl vinyl radical ($CH_3C{=}CH_2$) and CO_2 are the expected products of this channel, as shown in Scheme 2, thus suggesting that subsequent reactions of $CH_3C{=}CH_2$ must be the source of the additional observed CO. This postulate is the same as that of Orlando *et al.*[1] to explain high yields of CO formed when OH reacts with methacrolein in the presence of NO_x, in distinction to our experiments, as well as air (see Scheme 3). According to these workers, a fraction 0.65 of $CH_3C{=}CH_2$ leads to the formation of CO. The yield of HCl shows that a fraction 0.18 of the reaction proceeds *via* abstraction of a hydrogen, so that a yield of CO of 0.65 × 0.18 = 0.12 might be anticipated from the reactions of $CH_3C{=}CH_2$. There is thus an excess of 0.17 of the observed yield of CO over that accounted for by the known chemistry.

Scheme 3 shows that each $CH_3C{=}CH_2$ radical yields HCHO directly, at the same time as forming other radicals (CH_3, CH_3CO) that are indirect sources of HCHO. Since the yield of $CH_3C{=}CH_2$ is 0.18, the yield of HCHO could be 0.18 from the direct process and up to a further 0.18 from the indirect reactions. In reality, the yield of HCHO is 0.23. It follows that an amount of HCHO equivalent to a yield of 2 × 0.18 − 0.23 = 0.13 is not formed and/or is lost from the system.

In view of the similarity between the excess in yield of CO (0.17) and the deficit in HCHO (0.13), it is tempting to link the two observations. The obvious candidate for effecting the link, photolysis of HCHO, must probably be discounted. The integrated absorption cross section for Cl_2 is much larger than that for HCHO in our wavelength region, so that the UV doses used to drive the reaction could photolyse only *ca.* 1% of the HCHO. It may be, therefore, that the anomalous yields



Scheme 2



Scheme 3

of both CO and HCHO are related instead to the 'missing carbon' indicated by the overall carbon balance.

That a fraction of only 0.18 of the reaction between Cl and methacrolein proceeds *via* an abstraction channel may at first glance seem rather surprising. In apparent contrast, abstraction and addition in the reaction between OH radicals and methacrolein occur in the proportion 0.45 : 0.55.[1] However, these two sets of data seem in reality to be consistent with the known reactivities of the different species. The overall rate constants[23] and branching ratios[1] suggest a rate constant for the abstraction channel in the reaction of OH with methacrolein of 1.4×10^{-11} cm^3 molecule^{-1} s^{-1}. Where *only* abstraction can occur, as with acetaldehyde, Cl is about 4.5 times as reactive as OH.[17] If the same relative reactivity applies for methacrolein, the rate constant for the abstraction channel would be 6.3×10^{-11} cm^3 molecule^{-1} s^{-1}. Our rate constant (Table 3) for the overall reaction with Cl is 3.3×10^{-10} cm^3 molecule^{-1} s^{-1}. Thus, the predicted branching ratio into the abstraction channel would be 6.3/33 = 0.19, very close to the observed value of 0.18.

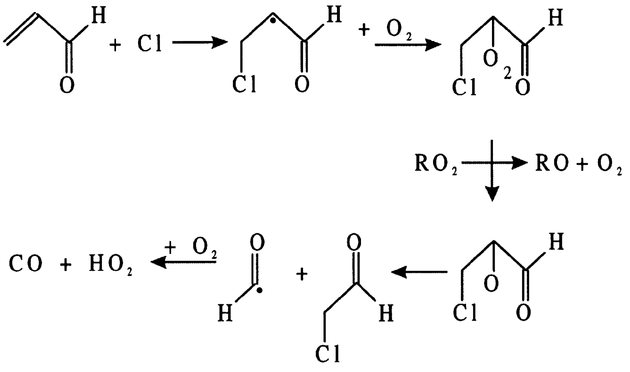
Acrolein. Scheme 4 illustrates a possible mechanism by which the observed products chloroacetaldehyde and CO could be formed following reaction (1) between Cl and acrolein. Formyl chloride, an oxidation product of the CH_2Cl radical, was not observed, so that the chloroalkoxy radical in the scheme evidently reacts predominantly as indicated, rather than to yield CH_2Cl and glyoxal. Formaldehyde, an observed product, may result either from the abstraction of the aldehydic hydrogen or from the addition of Cl to the more hindered end of the carbon–carbon double bond.

Approximately 0.5 of the reaction of OH radicals with acrolein proceeds *via* abstraction.[23] With Cl atoms, 0.22 ± 0.13 of the reaction is abstraction, a value similar to that found for the reaction of Cl with methacrolein. The smaller fraction of abstraction for reaction with Cl rather than OH probably again reflects a large rate constant for addition of Cl rather than some more fundamental difference in the abstraction by OH and Cl.

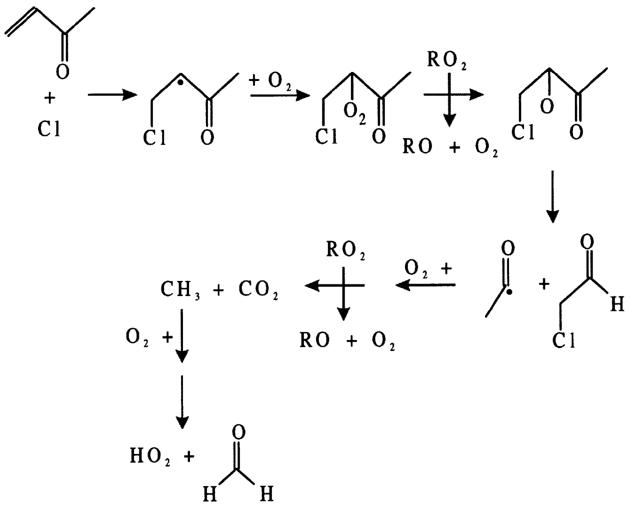
Methyl vinyl ketone. The formation of chloroacetaldehyde and formaldehyde following the reaction of Cl atoms with methyl vinyl ketone may be explained by a mechanism (Scheme 5) very similar to that for the corresponding reaction with acrolein.

Comparison with literature

A quantitative study of the products of reactions (1)–(3) has not yet been published. Fantechi *et al.*[24] have made an ancillary investigation of reactions (2) and (3), the reactions of Cl atoms with methacrolein and methyl vinyl ketone, as an aid to interpreting the products they observed from the reaction of Cl atoms with isoprene. The reactions were studied at ~740 Torr in synthetic air, but NO_x was present in the reaction chamber in these experiments, typical concentrations being 10 to 100 ppbv. The presence of NO_x is significant because in our work all peroxy radicals react with HO_2 and other peroxy species, rather than with NO, and the products may well not be identical. The presence of NO_x also allows for the possibility that potentially interfering OH radicals were formed by reaction of NO with HO_2 in the study of Fantechi *et al.*



Scheme 4



Scheme 5

The products observed by Fantechi *et al.*[24] for the reaction of Cl atoms with methacrolein (2) were methyl glyoxal, formyl chloride, formic acid, HCl, CO and CO_2. No chloroacetone was found. The extent of reaction (2) was not given by Fantechi *et al.* However, in the case of the reaction of Cl atoms with isoprene, the reaction was studied until the substrate had decayed to well below one-tenth of its initial concentration. It would seem likely that secondary products could thus be formed. Formyl chloride is an expected product from either the photolysis of chloroacetone or its reaction with atomic chlorine. Indeed, when the consumption of methacrolein was deliberately allowed to fall to below 30%, the yield of chloroacetone decreased and both formyl chloride and formic acid were observed. It seems possible, therefore, that the formyl chloride seen by Fantechi *et al.* is not a primary reaction product, but rather that it is formed in secondary reactions involving chloroacetone. Formic acid may be formed following the reaction of formaldehyde with HO_2.[25] Methyl glyoxal was not observed as a reaction product.

In reaction (3), the reaction of Cl atoms with methyl vinyl ketone, the products observed by Fantechi *et al.*[24] were chloroacetaldehyde, formic acid, formyl chloride, methyl glyoxal, CO and CO_2. The detection of chloroacetaldehyde agrees with the results of our study. The formic acid observed by Fantechi *et al.* may result from the reaction of formaldehyde with HO_2. Again, formyl chloride and methyl glyoxal were not observed as primary reaction products in our own study, although both the photolysis and the reaction with Cl of chloroacetaldehyde would be expected to yield formyl chloride. The reasons for the differences between our results and those of Fantechi *et al.* thus evidently merit further investigation.

Atmospheric implications

The first objective of our study in terms of atmospheric chemistry was to establish the correct rate coefficients for attack of Cl on the three α,β-unsaturated carbonyl compounds in order to determine the lifetimes of these species against attack by Cl in the marine boundary layer and to compare the lifetimes with those against attack by OH. The second major objective was to assess the possible impact of the products, especially the chlorinated ones, of the reactions.

The values of k_1 (acrolein) and k_3 (methyl vinyl ketone) obtained at low pressure (1.6 and 4.5 Torr) are less than those obtained at atmospheric pressure, indicating that the rate of the reactions are still dependent upon the total pressure within this range. The values obtained at atmospheric pressure, reported in this work in the case of reaction (1), and by Canosa-Mas *et al.*[14] in the case of reaction (3), are thus the values recommended as those relevant to the lower atmosphere.

The reactions of Cl atoms with the α,β-unsaturated carbonyl compounds yields mainly chlorinated organic species, the addition : abstraction ratio with both methacrolein and acrolein being approximately 4 : 1; in the case of methyl vinyl ketone, abstraction accounts for less than 3% of the overall reaction. The reaction of Cl atoms with methacrolein leads to the formation of chloroacetone, whilst reaction with both methyl vinyl ketone and acrolein leads to the formation of chloroacetaldehyde.

The importance of reactions (1)–(3) in the marine boundary layer (MBL) as both a sink for the organic compounds and a source of chlorinated organic species depends upon the concentration of Cl atoms and the rates of other possible loss processes. The other likely loss processes for the α,β-unsaturated carbonyl compounds are reaction with OH, O_3, NO_3, photolysis and wet deposition. The loss of methacrolein and methyl vinyl ketone from the gas phase into the liquid phase has been shown[26] to be too slow for wet deposition to be a major loss route. The photolysis of the two compounds has been shown[27] to be only of minor importance compared to reaction with OH radicals, as has the loss due to NO_3 and O_3. The lifetimes of acrolein, methacrolein, and methyl vinyl ketone with respect to oxidation by Cl atoms is thus most interestingly compared to the lifetimes with respect to oxidation by OH radicals.

The atmospheric concentration of Cl atoms is not known with any certainty, and it is probably very variable with respect to both time and location. The concentrations of Cl atoms and OH radicals used to calculate the lifetimes of the species with respect to loss by these oxidants are those proposed by Wingenter *et al.*,[28] based on the measurement of nonmethane hydrocarbons and halocarbons in the North Atlantic. The values, 3.3×10^4 and 0.3×10^6 molecule cm^{-3} for Cl atom and OH radical concentrations, correspond to the average values during the first five hours after dawn. The rate constants used for the reactions involving OH radicals are those recommended by Atkinson.[29] Table 5 shows the lifetimes calculated for these conditions. While it should be recognized that the [Cl] : [OH] ratio is unusually high under these circumstances, it is evident that in at least some parts of the MBL attack on the three α,β-unsaturated carbonyl compounds by Cl atoms can add substantially to, and perhaps even nearly double, the losses in reaction with OH.

The investigations that we have made of the products and of their yields have demonstrated that a greater fraction than expected of these reactions proceeds *via* addition, and thus formation of chlorinated organic species, than *via* H-abstraction, and thus direct formation of HCl. The potential impact of this finding on the atmosphere depends, of course, on the lifetimes and degradation products of the organic species. The key compounds in this respect are chloroacetaldehyde and chloroacetone. Chloroacetaldehyde is readily photolysed in the troposphere, its lifetime with respect to photolysis being ∼4.3 h.[30] Chloroacetone has a longer tropospheric lifetime, of the order of a few days; however, its main loss route is still expected to be photolysis.[19] In both cases, formyl chloride is the expected chlorinated oxidation product. The atmospheric fate of formyl chloride remains somewhat ambiguous, but it is likely that most will be lost by hydrolysis, leading to the formation of CO and HCl.[31] Thus the conclusion of this part of our study is that attack by Cl on the selected α,β-unsaturated carbonyl species will lead to the fairly rapid release to the atmosphere of HCl rather than of some longer lived and potentially noxious halogenated compounds.

Table 5 Lifetimes against atmospheric attack by Cl atoms and OH radicals. Assumed concentrations: $[Cl] = 3.3 \times 10^4$ molecule cm^{-3} and $[OH] = 0.3 \times 10^6$ molecule cm^{-3} (ref. 28)[a]

Compound	τ_{Cl}/h	τ_{OH}/h	τ_{OH}/τ_{Cl}
Acrolein	38	49	1.3
Methacrolein	26	29	1.1
Methyl vinyl ketone	40	52	1.3

[a] Note: the average [Cl] and [OH] on which these calculations are based refer to periods of five hours, far less than the values of τ obtained. The lifetimes quoted in the table must therefore be treated with caution, because they are really inverse rate constants for the five-hour average concentrations after dawn.

Enormous quantities of isoprene are converted to methacrolein in the atmosphere, and we have now shown that several channels of oxidation following initial attack by Cl on methacrolein lead to the formation of CO, with an overall yield of ∼0.75. The upper estimate of the release rate for isoprene is 503×10^9 kg C yr^{-1} (equivalent to $\sim 1174 \times 10^9$ kg yr^{-1} of CO for 100% conversion), while the natural contribution to CO release is thought to be about 430×10^9 kg yr^{-1}.[32] Thus, attack on methacrolein by Cl (and probably OH as well) has the potential to make a significant addition to the atmospheric burden of CO.

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